PB85-157378

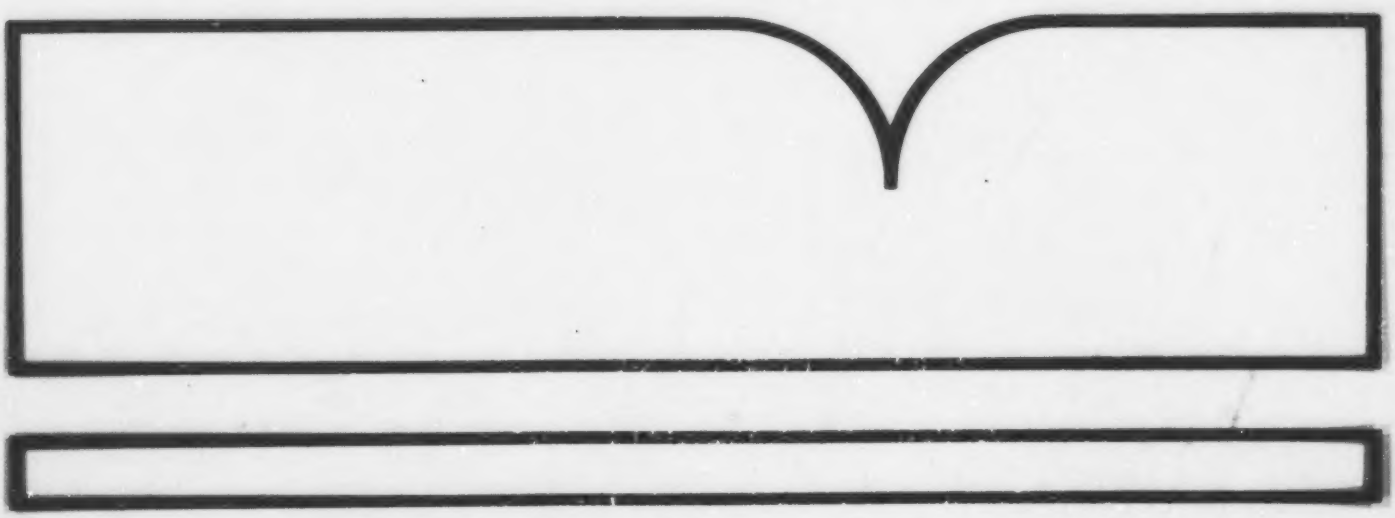
Computer Controlled Acquisition of Corrosion Rate Data from Multiple Sensors

Rockwell International, Thousand Oaks, CA

Prepared for

Environmental Protection Agency
Research Triangle Park, NC

Jan 85



U.S. Department of Commerce
National Technical Information Service
NTIS

PB85-157378

EPA/600/D-85/018
January 1985

COMPUTER CONTROLLED ACQUISITION OF CORROSION RATE DATA FROM MULTIPLE SENSORS

by

M. Kendig, S. Jeanjaquet, and F. Mansfeld
Rockwell International Science Center
Thousand Oaks, CA 91360

EPA Contract 68-02-3741

EPA Project Officer
Fred H. Haynie

ATMOSPHERIC SCIENCES RESEARCH LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
RESEARCH TRIANGLE PARK, NC 27711

REPRODUCED BY
NATIONAL TECHNICAL
INFORMATION SERVICE
U.S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA. 22161

TECHNICAL REPORT DATA (Please read Instructions on the reverse before completing)		
1. REPORT NO. EPA/600/D-85/018	2.	3. RECIPIENT'S ACCESSION NO. PB85 157378/AS
4. TITLE AND SUBTITLE COMPUTER CONTROLLED ACQUISITION OF CORROSION RATE DATA FROM MULTIPLE SENSORS		5. REPORT DATE January 1985 6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) M. Kendig, S. Jeanjaquet and F. Mansfeld		8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS Rockwell International Science Center 1049 Camino Dos Rios Thousand Oaks, CA 91360		10. PROGRAM ELEMENT NO. CDTA1D/06-2067 (FY-85) 11. CONTRACT/GRANT NO. 68-02-3741
12. SPONSORING AGENCY NAME AND ADDRESS Atmospheric Sciences Research Laboratory - RTP, N.C. Office of Research and Development U.S. Environmental Protection Agency Research Triangle Park, North Carolina 27711		13. TYPE OF REPORT AND PERIOD COVERED 14. SPONSORING AGENCY CODE EPA/600/09
15. SUPPLEMENTARY NOTES		

16. ABSTRACT

Determination of the polarization resistance from multiple sensors under computer control provides rapid, reproducible and accurate means for determining corrosion rates ranging over many orders of magnitude for large test matrices. Computerized techniques can simultaneously evaluate the response of many sensors to variations in the composition of a corrosive environment. Examples are presented of computerized corrosion monitoring of atmospheric corrosion rate monitors subjected to pollutant transients, and of materials in simulated flue gas desulfurization media containing trace elements.

17. KEY WORDS AND DOCUMENT ANALYSIS		
a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
18. DISTRIBUTION STATEMENT RELEASE TO PUBLIC	19. SECURITY CLASS (This Report) UNCLASSIFIED 20. SECURITY CLASS (This page) UNCLASSIFIED	21. NO. OF PAGES 18 22. PRICE

EPA Form 2220-1 (Rev. 4-77) PREVIOUS EDITION IS OBSOLETE

NOTICE

This document has been reviewed in accordance with U.S. Environmental Protection Agency policy and approved for publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

COMPUTER CONTROLLED ACQUISITION OF CORROSION RATE DATA FROM MULTIPLE SENSORS

M. Kendig, S. Jeanjaquet and F. Mansfeld

Rockwell International Science Center
Thousand Oaks, CA 91360

ABSTRACT

Determination of the polarization resistance from multiple sensors under computer control provides rapid, reproducible and accurate means for determining corrosion rates ranging over many orders of magnitude for large test matrices. Computerized techniques can simultaneously evaluate the response of many sensors to variations in the composition of a corrosive environment. Examples are presented of computerized corrosion monitoring of atmospheric corrosion rate monitors subjected to pollutant transients, and of materials in simulated flue gas desulfurization media containing trace elements.

INTRODUCTION

Methods have been developed in this laboratory to accumulate large quantities of corrosion rate data. A corrosion monitoring system used for evaluating the behavior of a number of different metals must measure corrosion rates which may range over several orders of magnitude for a given environment. This has been accomplished by multiplexing the response for a number of multiple two-electrode polarization resistance sensors to a single potentiostat having an autoranging current amplifier. A computer sequentially records and evaluates data from the response of the sensors to potential pulses. This approach has been applied to a test matrix for evaluating the effects of variatoons of flue gas desulfurization environments on a number of materials.

Alternatively, tests involving multiple cells subjected to an environment which varies with time require an automated corrosion monitoring method that can collect corrosion rate data simultaneously from multiple two-electrode polarization resistance sensors. This approach has been used to measure and store the corrosion resistance, R_p, for a number of atmospheric corrosion rate monitors (ACRMs) responding to pollutant transients in laboratory experiments.

EXPERIMENTAL APPROACH

Sequential Measurements

Figure 1 shows a schematic of the computerized electrochemical system used to sequentially evaluate the polarization resistance of multiple test cells. The sequential system includes a HP 6940B multiprogrammer which controls the switching associated with each of the test cells and multiplexes the two identical test electrodes, W_1 and W_2 and, in some cases, a reference electrode, R_1, immersed in solution, and a two-electrode wet/dry sensor (W_1' and W_2') for each respective cell, as shown in Fig. 2, to the PAR Model 173 potentiostat. A HP 9825 desktop computer communicates with both the multiprogrammer and the computer controllable current amplifier (PAR Model 276) of the potentiostat.

Communication of the desktop computer with the multiprogrammer enables the computer to set the switches to the electrodes of each respective cell so as to allow for 'Standby' and 'Measure' states. A table of the switching states appears with a schematic of the test cell in Fig. 2. These configurations have been defined to fit a particular application requiring measurement of R_p for the immersed (W_1, W_2) and wet/dry electrodes (W_1' W_2'). Modification of the switching program has been easily made for other applications.

For the sequential measurement of five test materials in simulated flue gas desulfurization environments, the 'Standby' state shorts W_1 to W_2 and W_1' to W_2' and disconnects all electrodes from the potentiostat. The electrodes for each cell remain in this configuration unless they are being measured. During the measurement cycle, the open circuit potential of the coupled test electrodes, W_1 and W_2, are measured with respect to R_1, in which case mode 'Measure E' is activated for the Pth cell. For the polarization resistance measurement, the reference electrode does not take part in the measurement, and the the polarization resistance between W_1 and W_2 and then W_1' and W_2' is measured. The 'Measure 1' state switches out R_1 and connects W_1 and W_2 to the potentiostat, with W_2 serving as the combined auxiliary and reference electrode and W_1 serving as the nominal working electrode. A 'Measure 2' state for W_1' and W_2' accomplishes the same task for the wet/dry sensors.

Communication of the computer to the potentiostat through the Model 276 enables application of the programmed potential step to the test electrodes and collection of the resulting current transient under optimum gain and sampling rate. The current transient data can then be analyzed to determine the polarization resistance R_p with correction for the ohmic (IR) drop. This method has been used to evaluate the influence of a large number of trace elements on the corrosion behavior of various materials in simulated flue gas desulfurization (FGD) environments. Details of the test environments and electrode preparation appear elsewhere (1).

Simultaneous Measurements

The apparatus used to simultaneously collect the transients from a number of two-electrode corrosion sensors (Fig. 1) includes a HP 6940B multiprogrammer containing two D/A cards (D/A #1 and D/A #2), a multiplexing card (MUX) inputting to a high speed analog-to-digital monitoring card (A/D) and an eight channel sample-and-hold card (S/H) constructed in this laboratory. The S/H card enables simultaneous sampling of all eight two-electrode sensors at controlled time intervals. A HP 9825 desktop computer controls the application of the pulse and the analysis of the current transients (2). This method has been applied to the analysis of the response of a number of ACRMs pretreated in different ways and experiencing transients in the environmental variables such as UV radiation and concentration of SO_2, ozone and nitrogen oxide and relative humidity (% RH). Figure 3 shows a schematic of the ACRM.

Theoretical Considerations

A sufficiently small perturbation of potential, ΔE, about the open circuit potential, E_o, of a corroding metal produces a current response, ΔI. After sufficient time to establish steady-state,[3] the ratio of ΔE to ΔI defines the polarization resistance, R_p, of the corroding metal. This quantity, when normalized with respect to the area of the sample, relates inversely to the corrosion rate or corrosion current density, i_{corr}, according to the following equation:

$$i_{corr} = b_a b_b / (2.303\ R_p (b_a + b_b)) \quad , \qquad (1)$$

where b_a and b_b are the Tafel constants for the respective anodic and cathodic and polarization behavior. Equation (1) may be simplified as:

$$i_{corr} = B/R_p \quad , \qquad (2)$$

where B is a parameter having units of volts. The details of the relationships between small amplitude current response to an applied potential has been thoroughly reviewed (4). The computerized method described here has been developed for evaluating the polarization resistance of up to ten test electrodes. The system, however, may be easily expanded to include more electrodes.

For both the sequential and simultaneous methods for monitoring the corrosion resistance of multiple cells, the test cells are placed in a two-electrode 'Measure' configuration, whereby one electrode serves as a nominal working electrode and the other, identical electrode serves as both reference and auxiliary electrode. A baseline current is determined with 0 V applied across the electrodes, then a +20 mV pulse is applied for 2 min, followed by 2 min of zero applied potential. A new baseline is then determined before application of a negative 20 mV pulse of 2 min duration. Analysis of the transients collected for each pulse follows the pulse.

The analysis of the data for each pulse assumes a solution resistance, R_s, in series with a parallel combination of a double layer capacitance, C_p, and polarization resistance, R_p. In general, R_p equals R_{corr}. The current transient, I(t), responding to a stepped potential, ΔE, across this model of the electrochemical interface can be linearized with respect to time:

$$\text{Log}(I(t) - I_{ss}) = a_0 + a_1 t \quad , \tag{3}$$

where I_{ss} is the steady-state current and

$$R_p = (\Delta E/I_{ss}) - R_s \tag{4}$$

$$R_s = \Delta E/(I_{ss} + \exp(a_0)) \tag{5}$$

$$C_p = (R_s + R_p)/R_s R_p \, a_1 \quad . \tag{6}$$

I_{ss} is determined from the current transient data by determining that I(t) is stationary according to the procedure shown in Fig. 4. Accordingly, the steady-state current is the current occurring at the time where the slope of the current vs time curve drops to zero within the noise of the experiment. This point is determined from the slope S and standard deviation $\sigma(S)$ of the slope for small intervals over the current transient. S is taken to be statistically equal to zero when

$$S < 0.3 \cdot \sigma(S) \quad . \tag{7}$$

Using I_{ss}, the current transient may be linearized according to Eq. (3), and a linear least squares fit provides R_s and C_p according to Eqs. (4)-(6). Knowing R_s allows correction for solution resistance according to Eq. (4). Hence, R_p may be accurately determined, even in the presence of a rather high solution resistance.

In determining R_s and C_p, the program selects portions of the transient for analysis by deleting exceedingly short time points where the instrumental risetime interferes with the transient, and also does not consider points where I(t) is close to I_{ss}. In some cases there are not enough points where the transient signal is significant to accurately determine R_s and C_p. However, a diagnostic expressed as the number of points used for the transient analysis is output to a paper tape.

At the end of the measurement cycle for a given cell, the computer signals the multiprogrammer to return the electrodes to the coupled 'Standby' state. The parameters from the transient analysis and the time (in units of elapsed seconds into the test) read at the end of the analysis for each pulse are stored on a magnetic tape cassette. In addition to polarization and solution resistance, the open circuit potential, E_{corr}, for the coupled immersed electrodes, as measured against the two reference electrodes, is also stored. As a backup to the magnetic tape storage, the elapsed time, polarization resistance and open circuit potential with respect to the reference electrode, E_o, are

printed out on paper tape. Sufficient error recovery code is provided in the program to eliminate remotely occurring tape I/O errors.

The data collected on the magnetic tape can be transferred via the HP 9825 desktop computer to a VAX 11/780 mainframe for additional data analysis, display and eventual archival storage on 7 or 9 track magnetic tapes. The availability of the data on the VAX allows rapid access and evaluation of the data using remote terminals.

Validation

Validation of the method has involved testing a number of dummy cells listed in Tables 1 and 2. As can be seen from these tables, R_p ranges over four orders of magnitude from 10^2 to 10^6 Ω. In addition, for several of the cases shown in Table 2, R_s lies close to R_p such that an uncompensated measure of R_p would be in error.

As shown in Table 1, a close agreement of the measured values to the true values occurs for the cells having sufficiently long transients so as to provide more than 20 points for the transient analysis. However, several cells had such short transients that neither R_s nor C_p could be determined (cells 2, 7 and 10), or had considerable errors (cells 3 and 9). Nevertheless, R_p, as determined by the potential pulse amplitude divided by the final current, was sufficiently accurate for these cases (cells 2, 3, 7, 9 and 10). The data in Table 2 represents the results for a second run, and the data show that the measured values of R_p can be accurately obtained for either very high values of R_p (> 100K Ω) or for values falling within the range of R_s (cells 3 and 4 in Table 2). Despite some inaccuracies observed in C_p, R_p values are all calculated within 5% of the true value.

RESULTS

The sequential approach to corrosion monitoring is best applied to cases where the long-term behavior of a large number of specimens must be determined in a given test environment. The corrosion resistance, effective capacitance and open circuit potential, E_{corr}, for Ferralium 225, stainless steel type 317L, Hastelloy G3, Monit and Ti have been monitored over several days in solutions simulating flue gas desulfurization environments. The most important result obtained for this test matrix is the wide variation in the corrosion rates for a given alloy due to different combinations of trace elements in a given baseline environment, and the large differences of corrosion rates for the five alloys in a given test solution.

Details of the environments and these results appear elsewhere (1) Examples for the experimental data appear in Figs. 5-9. Figure 5 shows the time dependence of the inverse of polarization resistance, R_p^{-1}, for the five immersed alloys in the pH 4 test solution of 5000 ppm Mg as $MgSO_4$, 5000 ppm Na as Na_2SO_4, and 10000 ppm Cl as NaCl containing high impurity levels of F^- (1000 ppm), Br^- (500 ppm), NO_3^- (200 ppm), Ca^{2+}

(100 ppm), Cr (500 ppm) and Si (100 ppm), and low levels (1 ppm) for each of the following: I^-, PO_4^{3-} Cu^{2+}, Mo (IV), Al (III) and Fe (III). The final R_p values range from $\sim 10^7$ Ω for Hastelloy G3 to 10^3 Ω for Ti; in the latter case, activation of the Ti surface occurred on the first day of exposure with a drop of E_{corr} by ~ 0.5 V, as seen in Fig. 6. At this point in time, the corrosion rate of Ti, as measured by R_p^{-1} increases by a factor of 1000. This result demonstrates that short-term test of one day or less would miss important features of the corrosion behavior.

The corrosion behavior of Ti differs greatly between the several pH 4 FGD solutions containing different combinations of trace impurities. For example, in Fig. 7, R_p^{-1} for Ti in the baseline solution (#16) shows the lowest value, while solutions #1, #12 and #13 all show relatively high values of R_p^{-1} within a factor of 10 of each other at the end of the test. It is important to note that E_{corr} for the baseline data is very similar to the noble values for solutions #1, #12 and #16 (Fig. 8), despite the differences in corrosion rates. This illustrates the point that E_{corr} data do not provide a monitor of corrosion in all cases.

Examples for the corrosion behavior of the wet/dry electrodes are given in Fig. 9. The spikes in R_p^{-1}, which occur when the electrodes are dipped into the solution in the first three days and at the end of the test, are very obvious as are the differences in corrosion rates for the five alloys.

Figures 10-13 show the results from the simultaneous measurement technique. This method has been applied to a study of the influence of pollutant transients on atmospheric corrosion. Eight zinc ARCMs underwent transients of relative humidity (% RH), SO_2, NO_2 and ozone concentrations. All of the sensors were pretreated in a 1 mM solution of $CaCl_2$, allowed to dry, and were then exposed to the %RH cycle shown in Fig. 10. Sensors 1 and 2 contained carbonaceous particulates. R_p for the eight sensors showed changes in R_p which followed closely the changes of %RH.

Following the %RH cycle, the first four sensors were exposed to transients in SO_2 concentration, as shown in Fig. 11. The sensors not coated with carbonaceous particulates (No. 3 and 4) experienced the greatest decrease in R_p.

Sensors 1-6 were then exposed to NO_2, with the results shown in Fig. 12. NO_2 influences the corrosion behavior of the sensors, however, the NO_2 does not have a large effect on the ACRM response as the SO_2 transient.

Fluctuations in ozone concentration had little influence on the observed R_p for sensors 1-6, which had previously been exposed to SO_2 and NO_2, as well as for sensors 7 and 8, which had no previous exposure to pollutant and give the highest values of R_p during the ozone exposure test (Fig. 13).

These data show how a large amount of information can be generated by simultaneously observing the behavior of a number of samples having different histories and exposed to environmental transients lasting several hours each. %RH and SO_2 appear to have the largest effects on the corrosion behavior of the ACRMs. The presence of carbonaceous materials has a somewhat moderating effect in the case of the SO_2 transient, as well as the NO_2 transient. NO_2 appears to have a measurable effect on the corrosion rates of the ACMs in 90% RH. Ozone shows little or no influence on the corrosion behavior of the sensors, regardless of their history.

SUMMARY AND CONCLUSIONS

A system has been developed that uses a microprocessor to sequentially evaluate a polarization resistance with correction for the series solution resistance for a large number of cells, which have a wide range of corrosion rates. The method has been validated using dummy cells and most recently by comparison to ac impedance analysis for a real cell. The system can easily be adapted for a variety of applications, as demonstrated by the results presented in this paper. The system is relatively simple to operate. No initial gain settings are required of the operator. The data are accurately stored and can readily be transferred to a mainframe computer for display, analysis and archival storage. Specific results for materials in the FGD environment illustrate the superiority of measuring R_p rather than E_o for evaluating the corrosion rate of a material in a variety of differing environments, and significant changes of R_p with time demonstrates the necessity for long-term experiments which can be performed most economically under computer control. Large variations in R_p for different materials in a given environment necessitates the use of a current amplifier with either autoranging capability or computer controllable gain if a variety of materials are to be measured during a single test.

A method for simultaneously evaluating the corrosion rates of multiple sensors has enabled the rapid and accurate comparison of the response of a number of corroding ACMs to a systematically varying environment. This system relies on multiple sample-and-hold circuits that simultaneously collect and store current transients from multiple sensors responding to a single applied pulse.

These methods can be applied to a large number of systems. It is anticipated that the use of such methods for developing materials selection criteria, based on statistical analysis of a large amount of rapidly generated test data, will be used to a greater extent in the future.

Acknowledgement

This research was sponsored by the Rockwell International IR&D Program, Environmental Protection Agency, Contract No. 68-02-3741, and Electric Power Research Institute, Contract No. RP 1871-7.

REFERENCES

1. F. Mansfeld, S.L. Jeanjaquet, M. Kendig, D.O. Raleigh and K. Fertig, "The Effect of Trace Elements on Corrosion in Total Immersion and Wet/Dry Conditions," Paper No. 38, NACE '85, Boston (1985).

2. M.W. Kendig, S.L. Jeanjaquet and F. Mansfeld, Abstr. No. 477, The Electrochemical Society, Ext. Abstr. Vol. 83-2 (1983).

3. F. Mansfeld and M. Kendig, Corrosion 37, 545 (1981).

4. F. Mansfeld, "Polarization Resistance Techniques for Measuring Corrosion Currents," in Advances in Corrosion Science and Technology, vol. 6, p. 163, M. Fontana and R. Staehle, eds. (1976).

5. F. Mansfeld, "Development and Evaluation of an Instantaneous Atmospheric Corrosion Rate Monitor," Final Report, Contract 68-02-3711, Rockwell International Science Center, Dec. 1984.

Table 1

R_s, R_p and C_p Results for Dummy Cells

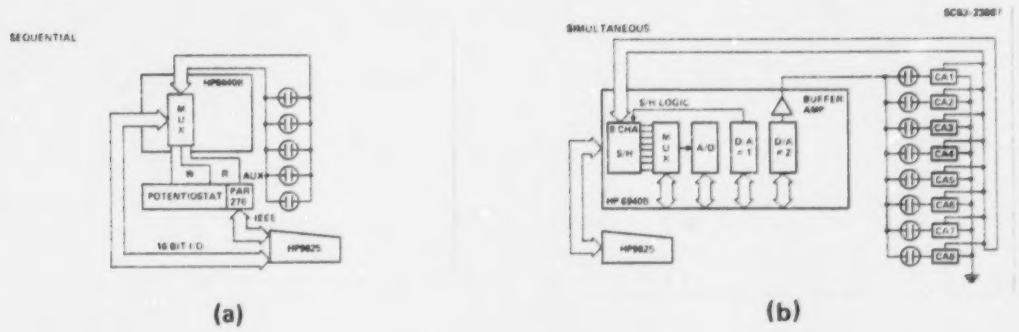
Cell No.	Dummy Cell Values			Calculated			No. Pts. where Transient is Significant
	R_s (Ω)	C_p (μF)	R_p (K Ω)	R_s (Ω)	C_p (μF)	R_p (K Ω)	
1	21.1	25	1.01	21.3	30	1.02	29
2	10^4	100	1000	n.d.	n.d.	950	0
3	30.5	10	0.997	74.9	12	1.036	8
4	30.5	100	100.3	31.0	119	104.6	38
5	23.2	100	10.47	24.0	108	10.48	10
6	25.1	100	1.002	25.7	113	1.002	84
7	23.1	1	99.6	n.d.	n.d.	102.3	0
8	22.1	25	98.9	22.0	28.3	102.8	26
9	23.1	100	98.2	23.2	127	101.4	10
10	30.7	1	0.999	n.d.	n.d.	1.039	0

Table 2

R_s, R_p and C_p Results for Dummy Cells

	Dummy Cell Values			Calculated		
Cell No.	R_s (Ω)	R_p (K Ω)	C_p (μF)	R_s (Ω)	R_p (K)	C_p (μF)
1	1000	1000	100	1017	959	116
2	40	1.12	2350	39.8	1.067	2031
3	50	0.098	2350	50.0	0.098	2310
4	36	0.264	1650	36.5	0.256	2111
5	2.1	10	100	8.8	9.7	99.8
6	5.4	1.0	68	7.5	1.05	77.0
7	1.1	98.6	10	n.d.	95.5	n.d.
8	21	101	27	n.d.	97.5	n.d.
9	2.1	100	1	n.d.	97.0	n.d.

Fig. 1 Schematic for the sequential (a) and simultaneous (b) corrosion monitoring approaches.



(a) (b)

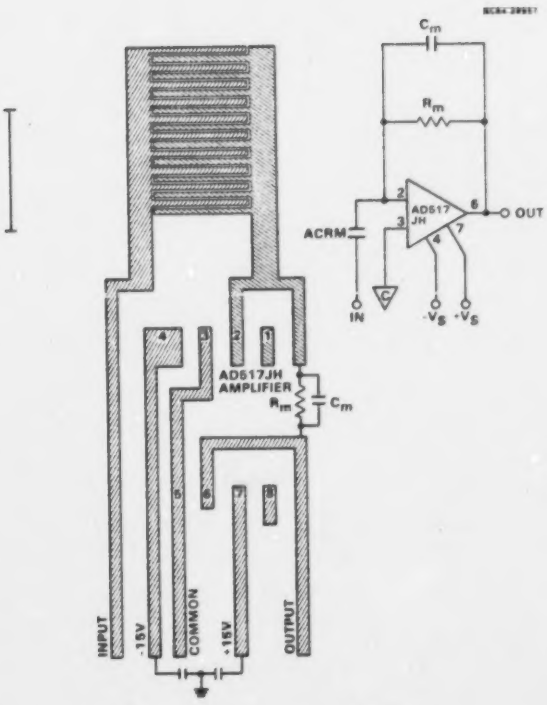
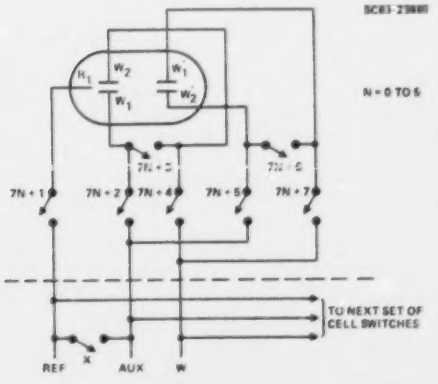


Fig. 3 Design of ACRM and electronic circuit.

Fig. 2 Switch control for sequential collection of data from combination liquid state and wet/dry sensors.



STATE	N = P							N ≠ P							
	7N + 1	7N + 2	7N + 3	7N + 4	7N + 5	7N + 6	7N + 7	7N + 1	7N + 2	7N + 3	7N + 4	7N + 5	7N + 6	7N + 7	X
STANDBY	1	0	1	0	0	1	0	0	0	1	0	0	1	0	0
MEASURE E(P)	1	0	1	1	0	1	0	0	0	1	0	0	1	0	0
MEASURE1* R(P)	0	1	0	1	0	1	0	0	0	1	0	0	1	0	1
MEASURE2** R(P)	0	0	1	0	1	0	1	0	0	1	0	0	1	0	1

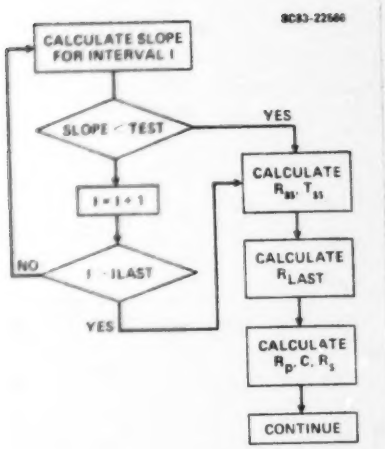


Fig. 4 Logic used for evaluating I_{ss}.

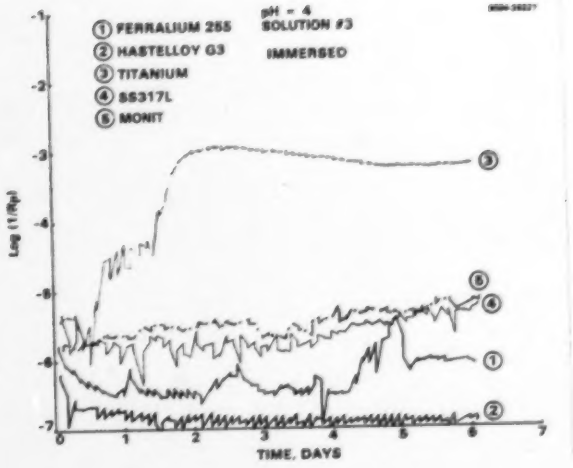


Fig. 5 Time dependence of R_p^{-1} for the materials in the pH 4 FGD solution.

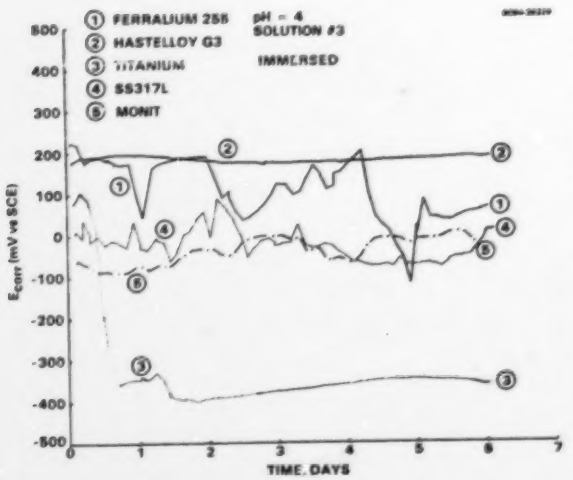


Fig. 6 Time dependence E_{corr} for the experiment in Fig. 5.

Fig. 7 Time dependence of R_p^{-1} for Ti immersed in several pH 4 FGD solutions containing different combinations of trace elements as described in Ref. 1.

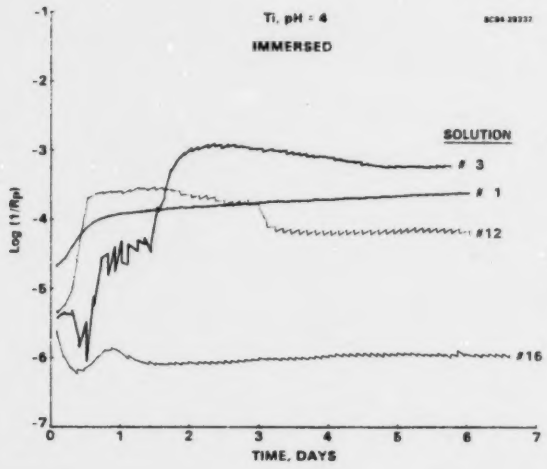


Fig. 8 Time dependence of E_{corr} for the experiments of Fig. 7.

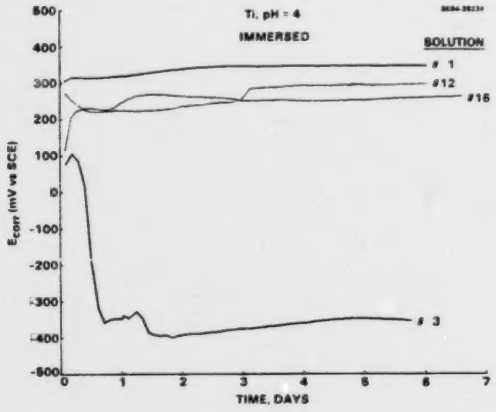
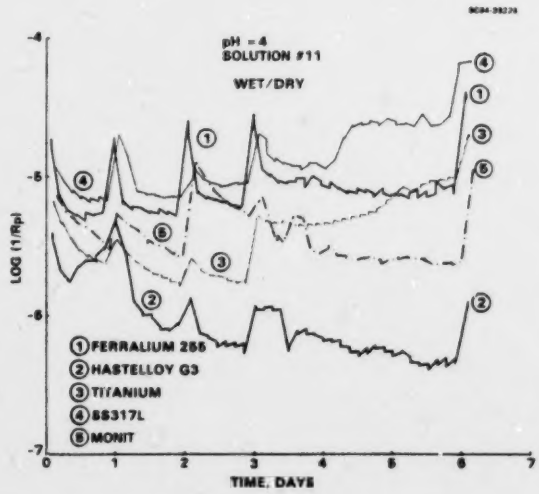


Fig. 9 Time dependence of R_p^{-1} for the wet/dry electrodes in solution #11 of Ref. 1.



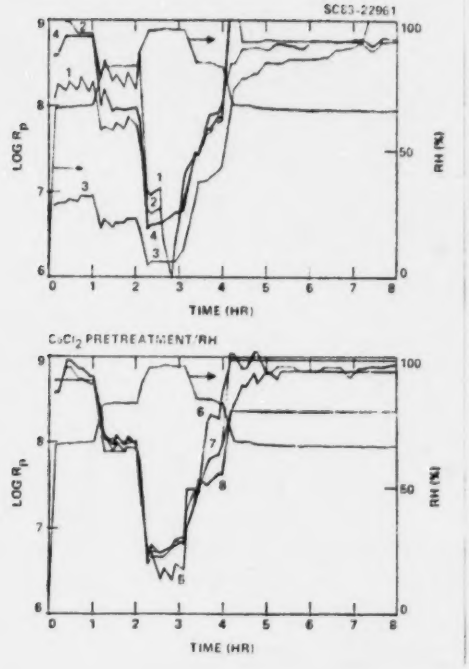


Fig. 10 Log R_p vs time for eight zinc ACRMs during a transient in the %RH.

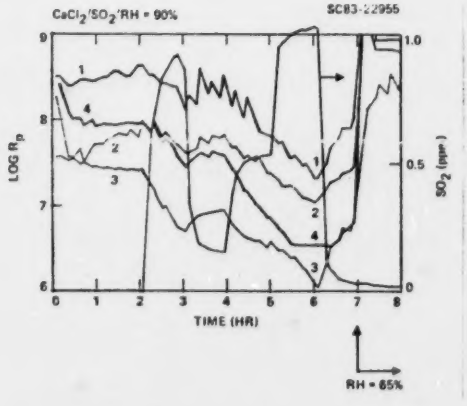


Fig. 11 Log R_p vs time for ACRMs during a transient in the SO_2 concentration.

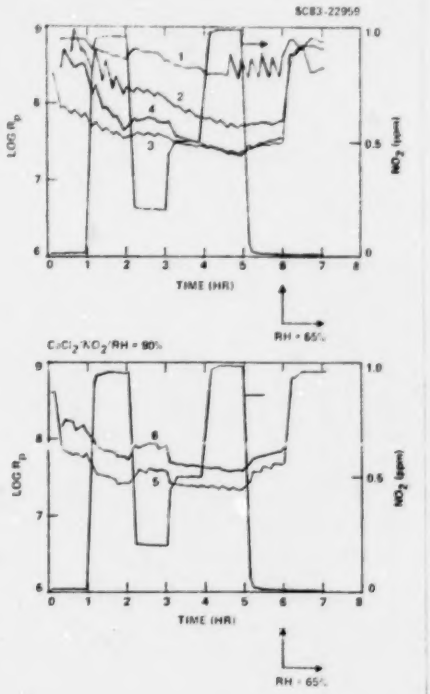


Fig. 12 Log R_p vs time for ACRMs during a transient in the NO_2 concentration.

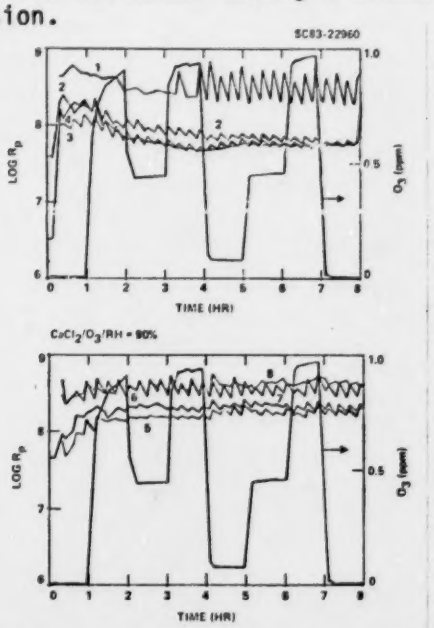


Fig. 13 Log R_p vs time for ACRMs during a transient in ozone concentration.